Recasting Ni-foam into NiF$_2$ nanorod arrays via a hydrothermal process for hydrogen evolution reaction application$^+$

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A promising electrode for hydrogen evolution reaction (HER) has been prepared via a reduction process to form NiF$_2$ nanorod arrays directly grown on a 3D nickel foam. We reveal NiF$_2$@Ni nanorod arrays for a stable hydrogen evolution reaction (HER) application. The computational analysis for H$_2$O, OH and H and experimentally in aqueous KOH endow considerable shift in Fermi levels for Ni (111) unlike for NiF$_2$ (110) on account of an effective coalition of $p$-orbitals of fluorine and $d$-orbitals of Ni in NiF$_2$. NiF$_2$ under pinning the reduced overpotential of 172 mV at 10 mA cm$^{-2}$ compared to Ni (242 mV) in same electrolyte. The electrocatalytic mechanism has been proposed using density functional theory (DFT) and is found in well accordance with the experimental findings of the present study. The preparation of self-grown porous nanostructured electrodes on the 3D nickel foam via a displacement reaction is possibly valuable for other metal halides for energy storage and conversion applications as these materials have inherently smaller overpotentials.

1. Introduction

Environmental pollution caused by using fossil fuels and the depletion of fossil fuels have pushed the world to the need of developing highly developed energy storage and conversion devices for clean and renewable energy technology.$^{1-4}$ Water electrolysis, nowadays, is attracting considerable attention of the researchers worldwide to produce hydrogen with numerous advantages such as elevated competence, profuse sources, easy-going environmental impact.$^{5-8}$ The generation of either hydrogen or oxygen through electrocatalytic water electrocatalyzers (EWCs) using electrochemical charge storage (ECS) devices as the voltage supply, which operate in tandem on solar panels would link together solar cell-energy storage-hydrogen production technology in a monolithic device. In this regard, researchers are working hard to explore electrocatalysts with high performance, which can improve the HER efficiency. The oxides of expensive and rare electrode materials such as Ir and Ru shows some of the best performance for water splitting$^{9-12}$ but are impractical for large scale use and do not offer comparable ability for each other’s use. On the contrary, the low efficiency of water dissociation due to the H$_2$O + Pt + e$^-$ → Pt-H + OH$^-$ reaction over the surface of Pt in an alkaline solution produces high overpotential and sluggish reaction kinetics. Regrettably, elevated cost and paucity in nature certainly limit the use of these electrocatalyst.

Consequently, for hydrogen production via water electrolysis for fuel cells, stable, efficient, and stump overpotential noble metal-free catalysts are urgently sought.$^{9-14}$ The comparison of the recently published reports on nickel-based electrocatalysts for EWC application using Ni(OH)$_2$, NiO, Ni$_3$S$_2$, NiSSe, NiTe, NiSe, etc., electrode materials prepared via chemical reduction and electro-less methods is displayed in Fig. 1.$^{15-26}$ The detailed performance comparison and related data have been provided in Table 1 of ESI.$^+$ The electrodes prepared by displacement/reduction/electroless progression by means of their high surface area and sturdy mechanical bonding with the substrate offer a superior performance than metal salt or binder-inspired electrode materials because elevated surface area renders numerous redox reactions, hopping-free charge transport pathway with least diffusion length and charge transfer resistance.$^{27-34}$ Nickel fluoride (NiF$_2$) with the rutile phase is an anti-ferromagnetic electrode material that shows weak ferromagnetic nature below the Néel point.$^{35}$ The preparation of the NiF$_2$ electrode is intricate up to some extend as the final products are not pure in phase tends to a
reduced performance. May be due to this we are not aware of any study on NiF$_2$ as an electrocatalyst.

Here, in the present study, the preparation of metal salt-based binder-free NiF$_2$ nanorod arrays (NAs) on a 3D nickel-foam (labeled as NiF$_2$@Ni) for EWC application is explored. The response of Ni and NiF$_2$ for the HER reaction was tested computationally via density functional theory (DFT) and supported experimentally via linear sweep voltammetry in a 0.1 M KOH electrolyte at room temperature (27 °C).

2. Experimental cognition

2.1 Chemicals used

Ethanol (C$_2$H$_6$O, 99%) and hydrofluoric acid (HF, 48%) were purchased from Artenano Company (labeled as NiF$_2$@Ni) for EWC application. Nickel foam (10 mm × 50 mm × 0.1 mm, 110 ppi (pores per inch) and mass (density of 320 g m$^{-2}$)) was purchased from Artenano Company Limited, Hong Kong.

2.2 Synthesis methodology

NiF$_2$@Ni NA was prepared via a simple and trouble-free one-step hydrothermal method. In detail, a 50 mL solution of HF (4 mL) was prepared in ethanol (46 mL) and poured into a Teflon-lined stainless-steel autoclave. A well-cleaned piece of Ni was inserted in this, and the autoclave was sealed properly. The sealed autoclave was heated at 120 °C for 12 h in an electric oven. Furthermore, the autoclave was allowed to cool to room temperature (27 °C) and then the NiF$_2$ deposited Ni was taken out. This NiF$_2$ deposited Ni was washed several times by distilled water and dried at 60 °C for 12 h under vacuum to get the final product as NiF$_2$@Ni NA.

2.3 Characterizations performed

The structural and morphological properties of both Ni and NiF$_2$@Ni NA were studied via X-ray diffraction (XRD, DB-Discovery Bruker, 40 kV, 40 mA, Cu K$_{\alpha}$, $\lambda$ = 1.5406 Å) and field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4800, at 15 kV) at an accelerating voltage equipped with energy dispersive X-ray spectroscopy (EDX) for elemental composition analysis. Transmission and high-resolution transmission electron microscopy (TEM and HR-TEM) measurements were performed using JEOL 2100F at 200 kV. Raman spectroscopy measurements of the as-prepared NiF$_2$@Ni NA surface were carried out using Xper Ram 200, NanoBase, Korea. The surface chemical composition and chemical bonding analysis was conducted via X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB250). The Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore-size distribution of the as-prepared electrode material was confirmed via nitrogen (N$_2$) adsorption/desorption isotherm confirmed using a Micromeritics ASAP2010 analyzer.

2.4 Electrochemical measurements

The linear sweep voltammetry (LSV) curves were obtained on an IVIUM electrochemical workstation system (IVIum Stat). All electrochemical measurements were carried out in a conventional three-electrode system, where Ni/NiF$_2$@Ni was used as the working electrode, Hg/HgO was used as the reference electrode and Pt was used as the counter electrode with a 0.1 M KOH aqueous electrolyte at room-temperature. The three-electrode system employed in the HER measurement with Hg/HgO was transferred into the RHE scale using a known conversion formula (see S1†).

2.5 Computational understanding

All calculations were done via the plane wave DFT method using the VASP5.4 program and plane wave set model. The Perdew–Burke–Ernzerh of exchange and correlation formalism along with the generalized gradient approach were applied. The cut-off energy of 400 eV and Gaussian electron smearing of 0.05 eV were used. The Brillouin zone was sampled with a $3 \times 3 \times 1$-k-point mesh for the four layered Ni (111) and $3 \times 2 \times 1$ for NiF$_2$ (110) surfaces before and after H$_2$O surface adsorption, and reactive –OH and –H species intermediates. The vacuum level of 15 Å was maintained in the z-direction so as to avoid any inter-surface interactions. The surface of NiF$_2$ (110) was unsaturated with a five coordinated –Ni centers, whereas Ni (111) possessed the Ni surface with nine immediate neighbors. Hence, the surface adsorption of the H$_2$O reactant and –OH and –H intermediates were noticed on Ni centers of the mentioned surface. The adsorption energies ($E_{\text{ads}}$) were calculated using the formula: $E_{\text{ads}} = E(X + \text{slab}) - E(X) - E(\text{slab})$, where $E(X + \text{slab})$, $E(X)$, $E(\text{slab})$ are total energies of slab with adsorbed species, pure species and pure slab, respectively (in the case of –H adsorption, $E(X)$ is taken as 0.5 × $E(H_2)$). The density of states (DOS) and band structure were confirmed at $9 \times 9 \times 3$ and $9 \times 6 \times 3$ k-point mesh for Ni (111) and NiF$_2$ (110) surfaces, respectively.

3. Results and discussion

3.1 Studies on the growth mechanism and morphology evolution

The pictorial presentation of the hydrothermal synthesis of the NiF$_2$@Ni NA is revealed in Fig. 2(a-c) with the original
photographs of spruce tree (Fig. 2d). The detailed reaction mechanism is described in supporting information section (Scheme S1†). The deposition of the NiF2@Ni NA has occurred on the surface of Ni foam by displacement reaction between NiO and F. From Fig. 2(e, f), the modifications in the surface of the nickel foam are clearly evidenced as the smooth surface turned into rough, swollen and spruce-type nano-arrays of the NiF2 with greenish colour suggesting; i) there could a strong bonding/adhesion between the product material and base Ni skeleton, and ii) Ni not only offered Ni ion source, but also acted as a flexible backbone to prevent NiF2 from agglomeration. Moreover, the flexibility of NiF2 electrode was also evidenced through bending test and shown in Fig. 2g. The corresponding FE-SEM image of the nickel foam before and after deposition of NiF2 is shown in Fig. 3(a, b–d). As shown in Fig. 3e and f, Ni and F are homogeneously distributed all over the nickel foam surface in the stoichiometric ratio of 1:2 to form NiF2@Ni NAs. The individual nanorod as clearly visible from the TEM image is shown in Fig. 3g. Each nanorod is grown with a broad-base and narrow tip with the size of 88–263 (±50) nm diameter and 500–1200 (±200) nm length. The interplanar spacing between the (110) and (111) planes were found to be 0.331 and 0.221 respectively, as revealed by the HR-TEM image (Fig. 3h).34,35 The nanocrystalline nature of the as-prepared NiF2@Ni NAs was confirmed by the selected area electron diffraction (SAED) pattern (Fig. 3i) in which the stretched diffraction spots from a single crystal pattern are observed. Moreover, from the SAED pattern, numerous relative orientations are also evidenced.

3.2. Structural elucidation

The deposition of NiF2 over the 3D nickel-foam was confirmed using XRD patterns, as revealed in Fig. 4a. The diffraction peaks for both NiF2 and Ni are observed. The diffraction planes (110), (101), (111), (210), (211), (220), (112) and (301) correspond to NiF2 and denoted by ‘♣’ (JCPDS no. 01-074-2140).33 Similarly, the diffractions peaks observed at 44.60°, 51.97° and 76.59° correspond to the (111), (200) and (220) planes of Ni and denoted as ‘Δ’ (JCPDS No. 01-070-0989),35,36 confirming the formation of NiF2 over 3D Ni. The Raman spectra of NiF2@Ni NAs is shown by Fig. 4b in which the two obvious peaks observed correspond to first-order optical LO phonon and second-order two-phonon modes of NiF2.37 Contradictorily, owing to the metallic nature, no peak is evidenced for the oxides of Ni in the Raman spectra.38

The surface area and corresponding pore-size distribution of NiF2@Ni NAs was studied via the nitrogen (N2) adsorption–desorption isotherm, as shown in Fig. 4c. The mesoporous and macroporous structures were confirmed from the N2 adsorption–desorption isotherm, which may occur from the hierarchical pore sizes observed in the 0.6–0.9 and 0.9–1.0 $P/\rho_o$ ranges.42 The specific surface area of the as-prepared electrode was found to be 25.10 m$^2$ g$^{-1}$ with corresponding pore diameters of 2.17 and 4.36 nm (inset of Fig. 4c), which is in well accordance with the higher surface area and multiple porosity of NiF2@Ni NAs (ESI, Fig. S1†).

3.3. XPS analysis

The surface electronic states of NiF2@Ni NAs were confirmed via XPS spectroscopy. The survey spectrum shows the peaks of Ni and F in Fig. 5a. The enlarged deconvoluted peak of Ni 2p...
reveals two spin–orbit doublets and two shake-up satellites (mentioned as ‘Sat.’) peaks. The spin orbit characteristics of Ni 2p were confirmed from the binding energy peaks at 856.2 and 876.3 eV for Ni 2p3/2 and Ni 2p1/2, respectively (Fig. 5b). The peak observed at 685.4 eV shows the F 1s core-level emission (Fig. 5c), which is in well accordance with the literature.38–42 Owing to electronegativity, the electron densities get transferred from Ni and F, which effect the peak position with slight shifting in the binding energies of Ni2p3/2, Ni2p1/2 and F1s.38

3.4 Water splitting: computational analysis and experimental findings

As mentioned earlier, the use of abundant and eco-friendly metal sulfides, perovskites, hydroxides and halide-based electrolytene catalysts for HER and OER through water splitting is being intensively sought. In our case, NiF2@Ni was also investigated for HER activity and compared with pristine Ni and previously reported self-grown electrode materials. To further understand the HER activity of Ni (111) and NiF2 (110), the adsorption energies and density of states (DOS) were obtained by a density functional theory (DFT) calculation, as provided in Fig. 6 and Fig. S2† respectively.

The tendency of NiF2 (110) towards H2O can be observed from Fig. 6 with the participation of two Ni centers on the surface, which leads to an adsorption energy of −0.21 eV. In case of Ni (111), only one Ni center was involved in H2O adsorption, providing a small adsorption energy of −0.19 eV with a rapid cascade in the Volmer step for NiF2 (110) unlike the Ni (111) surface. A more efficient water splitting mechanism is observed for NiF2 (110) as evidenced by stronger interactions of adsorbed −OH (−4.27 eV). Moreover, a large adsorption energy was found (−0.64 eV) for −H adsorption on the NiF2 (110) surface compared to −0.51 eV on the Ni (111) surface, suggesting the availability of active Ni centers and sufficient adsorption energies for intermediate OH and H adsorption that would provide superior HER activity at the NiF2 (110) surface.

The density of states (DOS) and projected DOS onto atomic level orbitals are given in Fig. S2 of ESL† The additional contribution of −F p-orbitals with d-orbitals from −Ni is clear from the total DOS of NiF2 (110), whereas only d-orbitals of −Ni were present in the Fermi level of Ni (111). This behavior did not alter even after the adsorption of H2O, OH or H intermediates on either surface. However, significantly larger shifts of the Fermi levels are noticed in Ni (111) compared to those in NiF2 (110), indicating the effective coalition of p-orbitals of −F and d-orbitals of −Ni in NiF2 (110). In short, the adsorption of water molecules with the hydrogen intermediate and desorption of OH ions from the surface of NiF2@Ni NA at the Volmer step suggest a stronger interaction with the water molecule, thereby enhancing its HER activity by decreasing the Tafel slope relative to that of Ni.

Inspired by our DFT calculations, the HER activities of NiF2@Ni NA and Ni electrodes were measured in 0.1 M KOH and are shown in Fig. 7a. We observed much lower onset over-potential for the NiF2@Ni NA electrode compared to that,
observed for Ni. The onset over-potential of 172 mV of NiF₂@Ni was much smaller than that of Ni (242 mV), which is attributed to a reduction in the energy barrier for the OH intermediate and stronger interactions with H₂O. Fig. 7b shows the Tafel slopes of 47 and 44 mV dec⁻¹ for Ni and NiF₂@Ni, respectively, at a current density of 10 mA cm⁻², suggesting the involvement of the Volmer step-controlled HER rate, where the H in an alkaline medium limits H adsorption, resulting in a lower surface coverage. These values are close to the theoretical Tafel slope of 30 mV dec⁻¹.⁴³,⁴⁴ These over-potentials are comparable with those reported in the literature and are provided in Table 1.¹⁷–²⁷ The diagrammatic comparison of the overpotential and Tafel slope of the NiF₂@Ni nanorod arrays has been shown in Fig. 7d, which indicates the superiority of the present study.

Stability is critical to electrocatalysts; therefore, we investigated the long-term stability of the NiF₂@Ni NA electrocatalyst by an amperometry measurement at a fixed potential for constant 10 mA cm⁻² (Fig. 7c) for 25 h, where the obtained data confirmed the good electrocatalytic durability of the NiF₂@Ni NA electrocatalyst, which is attributed to the strong adhesion interactions of NiF₂ on the Ni-Foam substrate.

4. Conclusions

A polycrystalline and mesoporous NiF₂@Ni NA electrocatalyst was successfully prepared on a 3D nickel foam via the hydrothermal method. The potential of the as-prepared electrocatalyst for HER was revealed in an aqueous electrolyte. The density functional theory calculations for Ni and NiF₂@Ni NA electrode surfaces supported better HER activity on the NiF₂ surface (with a smaller over-potential and Tafel slope) due to a stronger adsorption of H₂O molecules and desorption of OH⁻, compared to the Ni-foam surface. This was corroborated from the experimental measurements where NiF₂@Ni exhibits just 172 mV over-potential (with 44 mV dec⁻¹ Tafel slope), which is considerably smaller compared to Ni (242 mV with 47 mV dec⁻¹ Tafel slope) for HER at a current density of 10 mA cm⁻², suggesting a better water splitting performance for promoting HER. The DFT study well supports the reaction kinetics for the adsorption and desorption of H⁺ and hydrogen, which reveal the admirable HER activity. Producing self-grown hierarchically porous nanostructured electrodes on 3D metal foams by displacement reactions may be useful for other metal halides as electrodes for supercapacitors, supercapatteries, lithium-ion batteries, and HER/OER applications for materials that have intrinsically lower overpotentials for HER.

Conflicts of interest

There are no conflicts to declare.

References

5. J. Wang, S. Choi, J. Kim, S. W. Cha and J. Lim, Catalysts, 2020, 10(7), 770–792.